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(21)出願番号	特願平9-16526	(71)出願人	000004455 日立化成工業株式会社 東京都新宿区西新宿 2 丁目 1 番 1 号
(22)出願日	平成 9 年(1997) 1 月30日	(72)発明者	萩原 伸介 茨城県つくば市和台48 日立化成工業株式 会社筑波開発研究所内
(31)優先権主張番号	特願平9-6324	(72)発明者	斎藤 裕之 茨城県つくば市和台48 日立化成工業株式 会社筑波開発研究所内
(32)優先日	平 9 (1997) 1 月17日	(72)発明者	陶 晴昭 茨城県つくば市和台48 日立化成工業株式 会社筑波開発研究所内
(33)優先権主張国	日本 (J P)	(74)代理人	弁理士 若林 邦彦

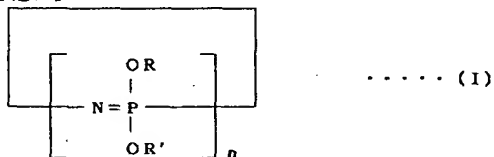
(54)【発明の名称】 電子部品封止用エポキシ樹脂成形材料及び電子部品

(57)【要約】

【課題】ノンハロゲン、ノンアンチモンで難燃化を達成でき、熱時硬度等の成形性が良好で、高温放置特性などの信頼性に優れた半導体封止用エポキシ樹脂成形材料を提供する。

【解決手段】(A) 1分子中に2個以上のエポキシ基を持つエポキシ樹脂、(B) 1分子中に2個以上のフェノール性水酸基を持つ化合物、(C) 次式 (I)

【化1】



(nは3～5の整数で、R、R' は同じでも異なってもよい炭素数1～4のアルキル基またはアリール基を示す)で示される環状ホスファゼン化合物、(D) 無機充填剤を必須成分とする成形材料であって、(C) 成分の含有量が充填剤(D)を除く配合成分の合計量に対し

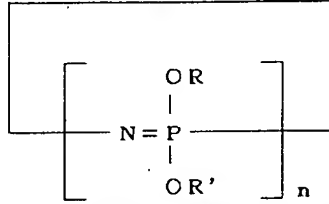
て燐原子の量が0.2～3.0重量%となる量であり、(D) 成分の含有量が成形材料全体に対して70重量%以上であることを特徴とする電子部品封止用エポキシ樹脂成形材料。

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## 【特許請求の範囲】

【請求項1】(A) 1分子中に2個以上のエポキシ基を持つエポキシ樹脂、(B) 1分子中に2個以上のフェノ\*



(nは3～5の整数で、R、R'は同じでも異なってもよい炭素数1～4のアルキル基またはアリール基を示す)で示される環状ホスファゼン化合物、(D)無機充填剤、を必須成分とする成形材料であって、(C)成分の含有量が充填剤(D)を除く配合成分の合計量に対して燐原子の量が0.2～3.0重量%となる量であり、(D)成分の含有量が成形材料全体に対して70重量%以上であることを特徴とする電子部品封止用エポキシ樹脂成形材料。

【請求項2】(C)成分のnが3である請求項1記載の電子部品封止用エポキシ樹脂成形材料。

【請求項3】(C)成分のn個のR及びn個のR'が全てフェニル基である請求項1または請求項2記載の電子部品封止用エポキシ樹脂成形材料。

【請求項4】(C)成分のn個のRとn個のR'のうち2～4個がヒドロキシフェニル基であり、他の全てがフェニル基である請求項1または請求項2記載の電子部品封止用エポキシ樹脂成形材料。

【請求項5】(C)成分のn個のR及びn個のR'が全てヒドロキシフェニル基である請求項1または請求項2記載の電子部品封止用エポキシ樹脂成形材料。

【請求項6】(A)成分のエポキシ樹脂が4,4'-ビス(2,3-エポキシプロポキシ)-3,3',5,5'-テトラメチルビフェニルである請求項1～5各項記載のいずれかの電子部品封止用エポキシ樹脂成形材料。

【請求項7】請求項1～6各項記載のいずれかの電子部品封止用エポキシ樹脂成形材料により素子を封止して得られる電子部品。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、半導体封止用エポキシ樹脂成形材料、特に環境対応の観点から要求されるノンハロゲン系の電子部品封止用エポキシ樹脂成形材料で、耐湿性、耐リフロークラック性など厳しい信頼性を要求されるVLSIの封止用に好適な成形材料及びその※

\* ー性水酸基を持つ化合物、(C)次式(I)  
【化1】

..... (I)

10※成形材料で素子を封止した電子部品に関する。

## 【0002】

【従来の技術】従来から、トランジスタ、ICなどの電子部品用素子の封止の分野ではエポキシ樹脂成形材料が広く用いられている。この理由としては、エポキシ樹脂が電気特性、耐湿性、耐熱性、機械特性、インサート品との接着性などの諸特性にバランスがとれているためである。これらのエポキシ樹脂成形材料の難燃化は主にテトラプロモビスフェノールAのジグリシジルエーテル等のブロム化樹脂と酸化アンチモンの組合せにより行われている。

## 【0003】

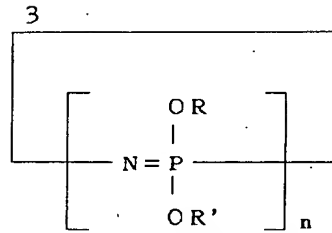
【発明が解決しようとする課題】近年、環境保護の観点からダイオキシンの問題に端を発し、デカブロムをはじめハロゲン化樹脂についても規制の動きがある。同様にアンチモン化合物も毒性面から規制の動きがあり、電子部品封止用エポキシ樹脂成形材料についても脱ハロゲン化(脱ブロム化)、脱アンチモン化の要求が出てきている。また、プラスチック封止ICの高温放置特性にブロムイオンが悪影響を及ぼすことが知られており、この観点からもブロム化樹脂量の低減が望まれている。本発明はかかる状況に鑑みなされたもので、高温保管特性の優れた電子部品封止用エポキシ樹脂材料を提供しようとするものである。

## 【0004】

【課題を解決するための手段】発明者らは上記の課題を解決するために鋭意検討を重ねた結果、難燃剤として特定の環状ホスファゼン化合物を配合することにより上記の目的を達成しうることを見だし、本発明を完成するに至った。

40 【0005】すなわち、本発明は、(1)(A)1分子中に2個以上のエポキシ基を持つエポキシ樹脂、(B)1分子中に2個以上のフェノール性水酸基を持つ化合物、(C)次式(I)

## 【化2】



..... (I)

(nは3～5の整数で、R、R'は同じでも異なってもよい炭素数1～4のアルキル基またはアリール基を示す)で示される環状ホスファゼン化合物、(D)無機充填剤を必須成分とする成形材料であって、(C)成分の含有量が充填剤(D)を除く配合成分の合計量に対して燐原子の量が0.2～3.0重量%となる量であり、(D)成分の含有量が成形材料全体に対して70重量%以上であることを特徴とする電子部品封止用エポキシ樹脂成形材料、(2)(C)成分のnが3である上記(1)記載の電子部品封止用エポキシ樹脂成形材料、(3)(C)成分のn個のR及びn個のR'が全てフェニル基である上記(1)または(2)記載の電子部品封止用エポキシ樹脂成形材料、(4)(C)成分のn個のRとn個のR'のうち2～4個がヒドロキシフェニル基であり、他の全てがフェニル基である上記(1)または(2)記載の電子部品封止用エポキシ樹脂成形材料、(5)(C)成分のn個のR及びn個のR'が全てヒドロキシフェニル基である上記(1)または(2)記載の電子部品封止用エポキシ樹脂成形材料、(6)(A)成分のエポキシ樹脂が4,4'-ビス(2,3-エポキシプロポキシ)-3,3',5,5'-テトラメチルビフェニルである上記(1)～(5)記載のいずれかの電子部品封止用エポキシ樹脂成形材料、(7)上記(1)～(6)記載のいずれかの電子部品封止用エポキシ樹脂成形材料により素子を封止して得られる電子部品、である。

#### 【0006】

【発明の実施の形態】本発明において用いられる(A)成分のエポキシ樹脂としては、電子部品封止用エポキシ樹脂成形材料で一般に使用されているもので特に限定はないが、たとえば、フェノールノボラック型エポキシ樹脂、オルソクレゾールノボラック型エポキシ樹脂をはじめとするフェノール類とアルデヒド類のノボラック樹脂をエポキシ化したもの、ビスフェノールA、ビスフェノールF、ビスフェノールS、アルキル置換ビフェノールなどのジグリシジルエーテル、ジアミノジフェニルメタン、イソシアヌル酸などのポリアミンとエポクロロヒドリンの反応により得られるグリシジルアミン型エポキシ樹脂、オレフィン結合を過酢酸などの過酸で酸化して得られる線状脂肪族エポキシ樹脂、及び脂環族エポキシ樹脂などがあり、これらを適宜何種類でも併用することができる。

【0007】上記に示したエポキシ樹脂の中で、4,4'-ビス(2,3-エポキシプロポキシ)-3,3',5,5'-

\*3',5,5'-テトラメチルビフェニルなどのアルキル置換ビフェノール型ジエポキシ樹脂を用いた場合、接着性、吸湿性が良好であり、これにより耐リフロークラック性及び耐湿性に優れた成形材料が得られる。このアルキル置換ビフェノール型ジエポキシ樹脂は、エポキシ樹脂全量に対し60重量%以上使用することが好ましい。60重量%未満では当該エポキシ樹脂の低吸湿性、高接着性の特長が発揮されず、本発明の目的である耐はんだ性に対して効果が小さい。当該エポキシ樹脂としては、4,4'-ビスヒドロキシ3,3',5,5'-テトラメチルビフェニルをエポクロロヒドリンを用いてエポキシ化して得られるものなどが上げられる。

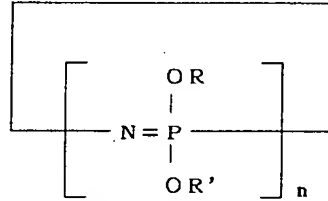
【0008】本発明において用いられる(B)成分の1分子中に2個以上のフェノール性水酸基を有する化合物としては、フェノール、クレゾール、キシレノール、レゾルシン、カテコール、ビスフェノールA、ビスフェノールFなどのフェノール類又はα-ナフトール、β-ナフトール、ジヒドロキシナフタレン等のナフトール類とホルムアルデヒド、アセトアルデヒド、プロピオンアルデヒド、ベンズアルデヒド、サリチルアルデヒド等のアルデヒド類とを酸性触媒下で縮合又は共縮合させて得られる樹脂、ポリバビニルフェノール樹脂、フェノール類とジメトキシパラキシレンから合成されるキシリレン基を有するフェノール・アラキル樹脂などがあり、単独又は2種類以上併用してもよい。

【0009】(A)成分のエポキシ樹脂と(B)成分のフェノール化合物の当量比((B)の水酸基数/(A)のエポキシ基数)は、特に限定はされないが、それぞれの未反応分を少なく抑えるために0.7～1.3の範囲に設定することが好ましい。

【0010】また、エポキシ樹脂とフェノール樹脂の硬化反応を促進する硬化促進剤を必要に応じて使用することができる。この硬化促進剤としては、例えば、1,8-ジアザビシクロ(5,4,0)ウンデセン-7などのジアザビシクロアルケン及びその誘導体、トリエチレンジアミン、ベンジルジメチルアミン、トリエタノールアミン、ジメチルアミノエタノール、トリス(ジメチルアミノメチル)フェノールなどの三級アミン類、2-メチルイミダゾール、2-フェニルイミダゾール、2-フェニル-4-メチルイミダゾール、2-ヘプタデシルイミダゾールなどのイミダゾール類、トリブチルホスフィン、メチルジフェニルホスフィン、トリフェニルホスフィンなどの有機ホスフィン類、テトラフェニルホスホニウム・テトラフェニルボレートなどのテトラ置換ホスホ

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ニウム・テトラ置換ボレート、2-エチル-4-メチルイミダゾール・テトラフェニルボレート、N-メチルモルホリン・テトラフェニルボレートなどのテトラフェニルボロン塩などがある。



(nは3~5の整数で、R、R'は同じでも異なってもよい炭素数1~4のアルキル基またはアリール基を示す)で示される化合物で、3量体の6員環、4量体の8員環、5量体の10員環を単独あるいは混合して用いることができる。エポキシ樹脂成形材料の流動性からは3量体を主成分として用いることが好ましい。

【0012】上記式(I)中のn個のR、R'は同じでも異なってもよい炭素数1~4のアルキル基またはアリール基で、たとえばnが3の3量体6員環の場合にはR、R'は6個の置換基となり、これらは全て同じでも異なってもよい。エポキシ樹脂成形材料の耐熱性、耐湿性の観点からはアリール基が好ましい。特にフ※

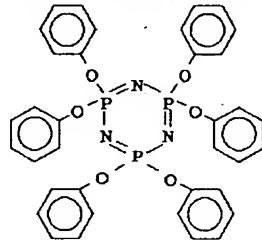
\*【0011】本発明において難燃剤として用いられる(C)成分の環状ホスファゼン化合物は、次式(I)【化3】

..... (I)

※エニル基であることが好ましく、さらに好ましくはヒドロキシフェニル基である。ヒドロキシフェニル基を導入する場合には、n個のRとn個のR'が全てヒドロキシフェニル基でも良いが、2~4個の導入が好ましい。ヒドロキシフェニル基の数が5個以上になるとエポキシ樹脂硬化物が脆くなりやすく、2個未満の場合にはエポキシ樹脂の架橋構造に取り込まれない成分がでてくるため、耐熱性が低下しやすい。

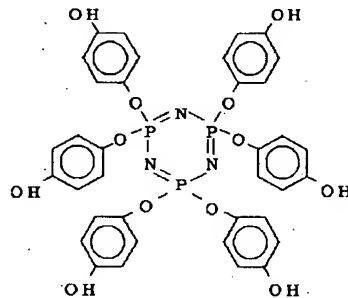
【0013】本発明において用いられる(C)成分の環状ホスファゼン化合物の好ましい構造として、たとえば、次の式(II)~(IV)

【化4】



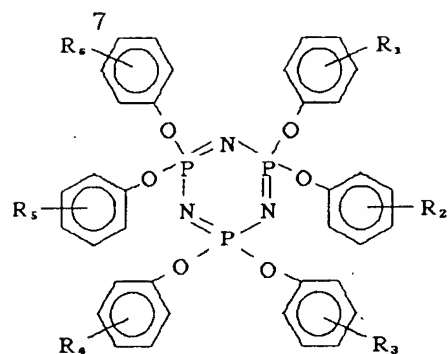
..... (II)

【化5】



..... (III)

【化6】



..... (IV)

(R<sub>1</sub>~R<sub>6</sub>のうち2~4個は水酸基で、他の4~2個は水素を示す)などがあげられる。

【0014】これらの環状ホスファゼン化合物の添加量は、充填剤を除く他の全配合成分に対して、0.2~3.0重量%の範囲内であることが必要である。0.2重量%より少ない場合は難燃効果が発揮されず、3.0重量%を超えた場合は耐湿性の低下を引き起こす。

【0015】本発明においては、(C)成分の特定の環状ホスファゼン化合物を用いることで信頼性、成形性の優れたノンハロゲン、ノンアンチモンの難燃性電子部品封止用エポキシ樹脂成形材料を提供するものである。炭化合物と窒素化合物の併用が難燃化に良いことは一般的に知られているが、本発明は優れた信頼性を発揮できる半導体封止用エポキシ樹脂成形材料の難燃剤成分として、炭原子と窒素原子の双方を構造中に含む化合物を提供するものである。

【0016】また、充填剤としては吸湿性低減及び強度向上の観点から無機充填剤を用いることが必要である。本発明における(D)成分の無機質充填剤としては、溶融シリカ、結晶シリカ、アルミナ、ジルコン、珪酸カルシウム、炭酸カルシウム、炭化珪素、窒化ホウ素、ベリリア、ジルコニア、などの粉体、又はこれらを球形化したビーズ、チタン酸カリウム、炭化珪素、窒化珪素、アルミナなどの単結晶繊維、ガラス繊維などを1種類以上配合して用いることができる。さらに、難燃効果のある無機充填剤としては水酸化アルミニウム、水酸化マグネシウム、硼酸亜鉛などが上げられ、これらを単独または併用して用いることもできる。無機質充填剤の配合量としては、吸湿性、線膨張係数の低減及び強度向上の観点から70重量%以上が好ましい。上記の無機充填剤の中で、線膨張係数低減の観点からは溶融シリカが、高熱伝導性の観点からはアルミナが好ましく、充填剤形状は成形時の流動性及び金型摩耗性の点から球形が好ましい。

【0017】その他の添加剤として高級脂肪酸、高級脂肪酸金属塩、エステル系ワックス、ポリオレフィン系ワックスなどの離型剤、カーボンブラックなどの着色剤、エポキシシラン、アミノシラン、ウレイドシラン、ビニルシラン、アルキルシラン、有機チタネート、アルミニウムアルコレートなどのカップリング剤などを用いるこ

\*とができる。

【0018】本発明における成形材料は、各種原材料を均一に分散混合できるのであれば、いかなる手法を用いても調製できるが、一般的な手法として、所定の配合量の原材料をミキサー等によって十分混合した後、ミキシングロール、押出機等によって熔融混練した後、冷却、粉碎する方法を挙げることができる。

【0019】リードフレーム、配線済みのテープキャリア、配線板、ガラス、シリコンウエハなどの支持部材に、半導体チップ、トランジスタ、ダイオード、サイリスタなどの能動素子、コンデンサ、抵抗体、コイルなどの受動素子等の素子を搭載し、必要な部分を本発明の封止用成形材料で封止して、電子部品を製造することができる。このような電子部品としては、たとえば、テープキャリアにバンパで接続した半導体チップを、本発明の成形材料で封止したTCPを挙げることができる。また、配線板やガラス上に形成した配線に、ワイヤーボンディング、フリップチップボンディング、はんだなどで接続した半導体チップ、トランジスタ、ダイオード、サイリスタなどの能動素子及び/又はコンデンサ、抵抗体、コイルなどの受動素子を、本発明の成形材料で封止したCOBモジュール、ハイブリッドIC、マルチチップモジュールなどを挙げることができる。電子部品を封止する方法としては、低圧トランスファー成形法が最も一般的であるが、インジェクション成形法、圧縮成形法等を用いてもよい。

【0020】

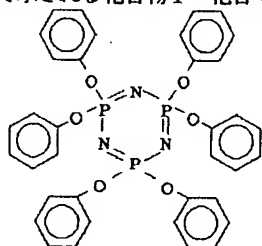
【実施例】次に実施例により本発明を説明するが、本発明の範囲はこれらの実施例に限定されるものではない。

【0021】実施例1~6

エポキシ当量200、軟化点67℃のクレゾールノボラック型エポキシ樹脂、エポキシ当量188、融点106℃のビフェニル骨格型エポキシ樹脂(4,4'-ビス(2,3-エポキシプロポキシ)-3,3',5,5'-тетрамethylビフェニル)、水酸基当量106、軟化点83℃のフェノールノボラック樹脂、水酸基当量167、軟化点70℃のフェノール・アラール樹脂(三井東圧製;ミレックスXL-225)、トリフェニルホスフィン、カルナバワックス、カーボンブラック、カップ

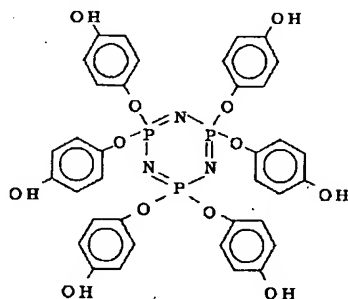
リング剤としてア-グリシドキシプロピトリメトキシ  
シラン、溶融シリカ、及び難燃剤として、本発明の  
(C)成分であり次の構造式で示される化合物1〜化合\*

\*物3  
【化7】



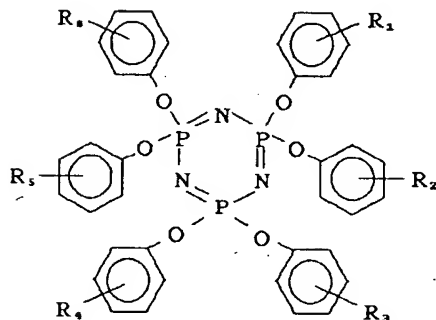
... 化合物1

【化8】



... 化合物2

【化9】



... 化合物3

(R<sub>1</sub>〜R<sub>6</sub>のうち3個は水酸基で他の3個は水素を示す)、を表1に示す重量比で配合し、混練温度80〜90℃、混練時間10分の条件でロール混練を行い、実施例1〜6の成形材料を作製した。

【0022】比較例1、2.

難燃剤としてエボキシ当量375、軟化点80℃、臭素※40

※含量48重量%のブロム化ビスフェノールA型エボキシ樹脂及び三酸化アンチモンを使用した以外は実施例と同様に、表1に示す配合で比較例1、2の成形材料を作製した。

【0023】

【表1】

表1

項目	実施例						比較例	
	1	2	3	4	5	6	1	2
グローバル/ホテック型エポキシ樹脂	100	100	100	-	-	-	85	-
ビフェニル骨格型エポキシ樹脂	-	-	-	100	100	100	-	85
ブロム化エポキシ樹脂	-	-	-	-	-	-	15.0	15.0
フェノール/ホテック樹脂	53.0	24.3	37.4	-	-	-	49.0	-
キシレン骨格樹脂	-	-	-	88.8	47.9	86.1	-	82.0
カルナウマス	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
三酸化アンチモン	-	-	-	-	-	-	10.0	5.0
カーボンブラック	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
カップリング剤	3.0	3.0	3.0	4.5	4.5	4.5	3.0	4.5
トリフェニルホスフィン	1.5	1.5	1.5	1.5	2.5	2.5	1.5	2.5
化合物1	37.0	-	-	35.0	-	-	-	-
化合物2	-	35.6	-	-	32.3	-	-	-
化合物3	-	-	36.4	-	-	33.6	-	-
溶融シリカ*1	594	504	545	1322	1081	1191	501	1119
充填剤量(重量)	75%	75%	75%	85%	85%	85%	76%	85%
焼成度(重量)*2	2.5%	2.5%	2.5%	2.0%	2.0%	2.0%	-	-

\* 1:平均粒径17.5 $\mu$ m、比表面積1.5m<sup>2</sup>/gの微粉状溶融シリカ

\* 2:充填剤を除く配合成分に対する溶剤の焼成度(重量百分率)

【0024】実施例及び比較例で得られた成形材料の特性を、次に示す方法で評価した。

(1) 熱時硬度

直径100mm、厚さ3mmの円板を成形する金型を使用し、トランスファプレスにて180 $\pm$ 3 $^{\circ}$ C、6.9 $\pm$ 0.17MPa、90秒の条件で成形材料を成形し、成形直後の成形品の熱時硬度をショア硬度計(Dタイプ)により求めた。なお、熱時硬度の値は数値が高いほど良いと評価する。

(2) 吸水率

JIS-K-6911に準拠した、直径50mm厚さ3mmの円板を作製し、85 $^{\circ}$ C、85%RHの条件で加湿

(3) 接着性

30 $\mu$ mのアルミ箔上に成形材料をトランスファプレスにて180 $\pm$ 3 $^{\circ}$ C、6.9 $\pm$ 0.17MPa、90秒の条件で成形し、その後、アルミ箔の90度方向へのピール強度を測定した。

(4) 難燃性

厚さ1/16インチの試験片を成形する金型を使用し、トランスファプレスにて180 $\pm$ 3 $^{\circ}$ C、6.9 $\pm$ 0.1\*

\* 7MPa、90秒の条件で成形材料を成形し、その後180 $\pm$ 5 $^{\circ}$ C、5時間後硬化を行った。評価はUL94-V0試験法に従った。

(5) 高温放置特性

外形サイズ5 $\times$ 9(mm)で5 $\mu$ mの酸化膜を有するシリコンサブストレート上にライン/スペースが10 $\mu$ mのアルミ配線を形成したテスト素子を使用して、部分銀メッキを施した42アロイのリードフレームに銀ペーストで接続し、サーモソニック型ワイヤボンダにより200 $^{\circ}$ Cで素子のボンディングパッドとインナリードをAu線にて接続した。その後、トランスファ成形により16ピン型DIP(Dual Inline Package)を作製し、得られた試験用ICを200 $^{\circ}$ Cの高温槽に保管し、所定時間毎に取り出して導通試験を行い、不良数を調べた。なお、評価用ICパッケージの成形はトランスファプレスにて180 $\pm$ 3 $^{\circ}$ C、6.9 $\pm$ 0.17MPa、90秒の条件で成形材料を成形し、その後180 $\pm$ 5 $^{\circ}$ C、5時間後硬化を行った。

【0025】得られた評価結果を表2に示す。

【表2】

表2

項目	実施例						比較例	
	1	2	3	4	5	6	1	2
熱時硬度	78.0	86.0	84.0	75.0	83.0	81.0	85.0	80.0
吸水率(72h)(%)	0.25	0.32	0.27	0.17	0.21	0.19	0.28	0.19
接着性(N/m)	350	250	330	780	580	720	310	720
難燃性:UL94	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0
高温放置特性 (不良数/母数)	200h	0/10	0/10	0/10	0/10	0/10	0/10	0/10
	400h	0/10	0/10	0/10	0/10	0/10	0/10	4/10
	600h	0/10	0/10	0/10	0/10	0/10	3/10	10/10
	800h	0/10	0/10	0/10	0/10	0/10	7/10	-

【0026】本発明の実施例1~6は、ブロム化樹脂及び50 $\mu$ m $\times$ 50 $\mu$ m $\times$ 50 $\mu$ mのアンチモン化合物を含む比較例1、2と較べ高温放置

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特性が格段に向上している。特に、実施例4～6はビフェニル骨格型エポキシ樹脂を使用しているため接着性も良好である。本発明の難燃剤を用いた実施例はいずれも高温放置特性が良好で、難燃性にも優れているが、化合物1はエポキシ基と反応可能な官能基を持たないため、これを難燃剤として用いた場合は実施例1及び4に示すように熱時硬度がやや低下する。また、化合物2は6個の置換基が全てエポキシ基と反応可能なヒドロキシフェニル基であるため、これを用いた実施例2及び5は硬化性は良好であるが、接着性がやや低下する。置換基のう

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ち3個がヒドロキシフェニル基である化合物3を使用した実施例3及び6は熱時硬度と接着性のバランスに特に優れる。

【0027】

【発明の効果】本発明によって得られる電子部品封止用エポキシ樹脂成形材料は実施例で示したようにノンハロゲン、ノンアンチモンで難燃化を達成でき、これを用いてIC、LSIなどの電子部品を封止すれば成形性が良好であり、耐湿性、高温放置特性などの信頼性に優れた製品を得ることができ、その工業的価値は大である。

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フロントページの続き(51)Int. Cl.<sup>6</sup>

識別記号

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H01L 23/31



**WEST**

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File: DWPI

Sep 29, 1998

DERWENT-ACC-NO: 1999-169826

DERWENT-WEEK: 199919

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TITLE: Epoxy! resin moulding material for sealing electronic components - comprises epoxy! resin, compound having at least two phenolic hydroxy groups, cyclic phosphazene compound and inorganic filler

PATENT-ASSIGNEE:

ASSIGNEE

HITACHI CHEM CO LTD

CODE

HITB

PRIORITY-DATA: 1997JP-0006324 (January 17, 1997)

PATENT-FAMILY:

PUB-NO

PUB-DATE

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JP 10259292 A

September 29, 1998

008

C08L063/00

APPLICATION-DATA:

PUB-NO

APPL-DATE

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DESCRIPTOR

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INT-CL (IPC): C08 G 59/00; C08 K 5/13; C08 K 5/5357; C08 L 63/00; H01 L 23/29; H01 L 23/31

ABSTRACTED-PUB-NO: JP 10259292A

BASIC-ABSTRACT:

A new epoxy resin moulding material for packaging of electronics components contains (A) an epoxy resin having at least two epoxy gps. per molecule, (B) cpd. having at least two phenolic hydroxyl gps. per one molecule, (C) a cyclophosphazene cpd. of formula (1), and (D) inorganic filler. The amt. of (C) is 0.2-0.3 wt.% in terms of phosphorus atom w.r.t. the total amt. of the components except (D). The amt. of (D) is at least 70 wt.% w.r.t. the total amt. of the moulding material. n = integer of 3-5; R, R' = 1-4C alkyl or aryl gp.

Electronics components sealed with the new epoxy resin moulding material are also claimed.

USE - For sealing or packaging electronics components including transistors or IC's.

ADVANTAGE - The new moulding material is non-flammable and is free of halogen and antimony. It has good mouldability, providing electronics components with higher damp-resistance and heat-resistance.

CHOSEN-DRAWING: Dwg.0/0

TITL E-TERMS: POLYEPOXIDE RESIN MOULD MATERIAL SEAL ELECTRONIC COMPONENT COMPRISE POLYEPOXIDE RESIN COMPOUND TWO PHENOLIC HYDROXY GROUP CYCLIC PHOSPHAZENE COMPOUND INORGANIC FILL

DERWENT-CLASS: A21 A92 A95 E11 L03 U11

CPI-CODES: A05-A01E2; A08-D; A08-F03; A08-R01; A11-B05; A12-E04; A12-E07C; E05-G04;  
E10-E02D; L04-C20A;

EPI-CODES: U11-A07; U11-E02A2;

CHEMICAL-CODES:

Chemical Indexing M3 \*01\*

Fragmentation Code

B615 B713 B720 B730 B732 B815 B833 B840 F012 F014  
F016 F018 F019 F580 G001 G002 G010 G011 G012 G013  
G019 G020 G021 G022 G029 G040 G100 G111 G112 G113  
G221 G299 H401 H402 H403 H404 H405 H441 H442 H443  
H444 M121 M122 M124 M129 M148 M149 M210 M211 M212  
M213 M214 M231 M232 M233 M272 M280 M281 M282 M283  
M320 M411 M510 M521 M530 M531 M532 M533 M540 M620  
M781 M903 M904 Q130 Q454

Ring Index

07756 07783 09796

Markush Compounds

199915-EQ701-K 199915-EQ701-U

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: C1999-049898

Non-CPI Secondary Accession Numbers: N1999-123922

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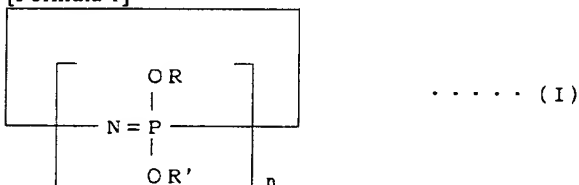
CLAIMS

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[Claim(s)]

[Claim 1] (A) The epoxy resin which has two or more epoxy groups in 1 molecule, the compound which has two or more phenolic hydroxyl groups in (B) 1 molecule, the (C) following formula (I)

[Formula 1]



the annular phosphazene compound shown by (n is the integer of 3-5 and R and R' shows the alkyl group or aryl group of carbon numbers 1-4 which may be different even if the same) -- (D) It is the molding material which uses an inorganic bulking agent as an indispensable component, and the content of the (C) component is an amount from which the amount of a phosphorus atom becomes 0.2 - 3.0 % of the weight to the total quantity of the combination component except a bulking agent (D). (D) Epoxy resin molding compound for electronic-parts closure to which the content of a component is characterized by being 70 % of the weight or more to the whole molding material.

[Claim 2] (C) The epoxy resin molding compound for electronic-parts closure according to claim 1 whose n of a component is 3.

[Claim 3] (C) The epoxy resin molding compound for electronic-parts closure according to claim 1 or 2 all of n R of a component and whose n R' are phenyl groups.

[Claim 4] (C) The epoxy resin molding compound for electronic-parts closure according to claim 1 or 2 other all of whose 2-4 in n R of a component and n R' are a hydroxyphenyl machine, and are phenyl groups.

[Claim 5] (C) The epoxy resin molding compound for electronic-parts closure according to claim 1 or 2 all of n R of a component and whose n R' are hydroxyphenyl machines.

[Claim 6] (A) The epoxy resin molding compound for electronic-parts closure of the claim 1 whose epoxy resin of a component is a - screw (2, 3-epoxy propoxy) -3, 3', and 4 and 4 '5, 5'-tetramethyl biphenyl - 5 each term publication either.

[Claim 7] Electronic parts which close an element by the epoxy resin molding compound for electronic-parts closure of a claim 1 - 6 each term publication either, and are obtained.

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[Translation done.]

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This inventions are an epoxy resin molding compound for semiconductor closure, especially the epoxy resin molding compound for electronic-parts closure of the non halogen system demanded from a viewpoint of environmental correspondence, and relate to the electronic parts which closed the element by the suitable molding material for closure of VLSI of which severe reliability, such as moisture resistance and reflow-proof crack nature, is required, and its molding material.

[0002]

[Description of the Prior Art] From the former, the epoxy resin molding compound is widely used in the field of closure of elements for electronic parts, such as a transistor and IC. As this reason, it is because the epoxy resin maintains balance in many properties, such as an electrical property, moisture resistance, thermal resistance, a mechanical characteristic, and an adhesive property with an insertion article. Flameproofing of these epoxy resin molding compounds is mainly performed by the combination of bromine-ized resins, such as diglycidyl ether of tetrabromobisphenol A, and an antimony oxide.

[0003]

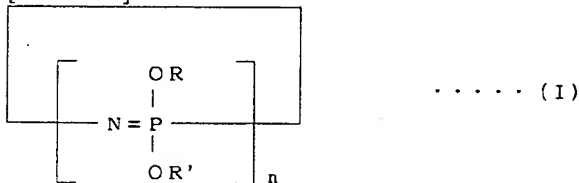
[Problem(s) to be Solved by the Invention] In recent years, it stems from the problem of dioxin from a viewpoint of environmental protection, a deca bromine is begun, and there is movement of regulation also about a halogenation resin. Similarly, an antimony compound also has the movement of regulation from a toxic field, and the demand of dehalogenation-izing (debromination) and the formation of \*\* antimony is coming out of it about the epoxy resin molding compound for electronic-parts closure. Moreover, it is known that bromine ion will have a bad influence on the elevated-temperature neglect property of the plastics closure IC, and reduction of the amount of bromine-ized resins is desired also from this viewpoint. this invention was made in view of this situation, and tends to offer the epoxy resin material for electronic-parts closure which was excellent in the elevated-temperature storage property.

[0004]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, as a result of repeating examination wholeheartedly, by blending a specific annular phosphazene compound as a flame retarder, artificers find out that the above-mentioned purpose can be attained and came to complete this invention.

[0005] That is, this invention is the epoxy resin which has two or more epoxy groups in (1) (A) 1 molecule, the compound which has two or more phenolic hydroxyl groups in (B) 1 molecule, and the (C) following formula (I).

[Formula 2]



the annular phosphazene compound shown by (n is the integer of 3-5 and R and R' shows the alkyl group or aryl group of carbon numbers 1-4 which may be different even if the same) -- (D) It is the molding material which uses an inorganic bulking agent as an indispensable component, and the content of the (C) component is an amount from which the amount of a phosphorus atom becomes 0.2 - 3.0 % of the weight to the total quantity of the combination component except a bulking agent (D). (D) The epoxy resin molding compound for electronic-parts closure to which the content of a component is characterized by being 70 % of the weight or more to the whole molding material, (2) The epoxy resin molding compound for electronic-parts closure of the above-mentioned (1) publication whose n of the (C) component is 3, (3) The above (1) all of n R of the (C) component and whose n R' are phenyl groups, or the epoxy resin molding compound for electronic-parts closure given in (2), (4) 2-4 in n R of the (C) component and n R' are a hydroxyphenyl machine. The above (1) other all of whose are phenyl groups, or the epoxy resin molding compound for electronic-parts closure given in (2), (5) The above (1) all of n R of the (C) component and whose n R' are hydroxyphenyl machines, or the epoxy resin molding compound for electronic-parts closure given in (2), (6) One epoxy resin molding compound for electronic-parts closure of the above-mentioned (1) - (5) publications whose epoxy resins of the (A) component are - screw (2, 3-epoxy propoxy) -3, 3', and 4 and 4 '5, 5'-tetramethyl

biphenyls, (7) -- the electronic parts which close an element by one epoxy resin molding compound for electronic-parts closure of the above-mentioned (1) - (6) publications, and are obtained -- it comes out [0006]

[Embodiments of the Invention] As an epoxy resin of the (A) component used in this invention Although it is generally used by the epoxy resin molding compound for electronic-parts closure and there is especially no limitation, for example That which epoxidated the novolak resin of phenols including a phenol novolak type epoxy resin and an orthochromatic cresol novolak type epoxy resin, and aldehydes, Diglycidyl ether, such as bisphenol A, Bisphenol F, Bisphenol S, and alkylation biphenol, The glycidyl amine type epoxy resin obtained by the reaction of polyamine and epichlorohydrin, such as a diamino diphenylmethane and an isocyanuric acid the line oxidized and obtained by peroxy acids, such as a peracetic acid, in olefin combination -- there are an aliphatic epoxy resin, an alicycle group epoxy resin, etc., and any number of kinds of these can be suitably used together

[0007] In the epoxy resin shown above, when alkylation biphenol type diepoxy resins, such as a - screw (2, 3-epoxy propoxy) -3, 3', and 4 and 4 '5, 5'-tetramethyl biphenyl, are used, an adhesive property and hygroscopicity are good, and the molding material which was excellent in reflow-proof crack nature and moisture resistance by this is obtained. As for this alkylation biphenol type diepoxy resin, it is desirable to use it 60% of the weight or more to the epoxy resin whole quantity. At less than 60 % of the weight, the low hygroscopicity of the epoxy resin concerned and the feature of a high adhesive property are not demonstrated, but an effect is small to the solder-proof nature which is the purpose of this invention. What epoxidates a - screw hydroxy 3, 3', and 4 and 4 '5, 5'-tetramethyl biphenyl, using epichlorohydrin as the epoxy resin concerned, and is obtained is raised.

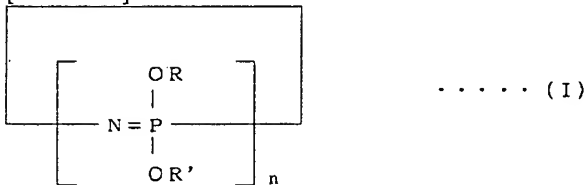
[0008] As a compound which has two or more phenolic hydroxyl groups in 1 molecule of the (B) component used in this invention A phenol, cresol, a xlenol, a resorcinol, a catechol, Phenols or alpha naphthols, such as bisphenol A and Bisphenol F, Naphthols, formaldehyde, such as a beta naphthol and dihydroxy naphthalene, Aldehydes, such as an acetaldehyde, a propionaldehyde, a benzaldehyde, and a salichlaldehyde, under an acid catalyst Condensation or the resin which is made to carry out copolycondensation and is obtained, there are PORIPA rabbi nil phenol resin, a phenol aralkyl resin which has the KISHIRIREN machine compounded from phenols and dimethoxy paraxylene, and independent -- or you may use two or more kinds together

[0009] (A) although especially limitation is not carried out for the equivalent ratio (the number of epoxy groups of number of (B) ] of hydroxyl groups/(A)) of the epoxy resin of a component, and the phenolic compound of the (B) component -- each -- unreacted -- a part -- in order to stop few, it is desirable to set it as the range of 0.7-1.3

[0010] Moreover, the hardening accelerator which promotes the hardening reaction of an epoxy resin and phenol resin can be used if needed. As this hardening accelerator, for example A diazabicyclo alkene and its derivatives, such as 1 and 8-diazabicyclo (5, 4, 0) undecene -7, A triethylenediamine, a benzyl dimethylamine, a triethanolamine, The third class amines, such as dimethylamino ethanol and a tris (dimethyl aminomethyl) phenol, 2-methyl imidazole, 2-phenyl imidazole, a 2-phenyl-4-methyl imidazole, Imidazole derivatives, such as 2-heptadecyl imidazole, tributyl phosphine, Organic phosphines, such as methyl diphenylphosphine and triphenyl phosphine Tetrapod substitution phosphonium tetrapod substitution borate, such as tetrapod phenyl phosphonium tetraphenyl borate, There are tetraphenylboron salts, such as 2-ethyl-4-methyl imidazole tetraphenyl borate and N-methyl morpholine tetraphenyl borate, etc.

[0011] The annular phosphazene compound of the (C) component used as a flame retarder in this invention is the following formula (I).

[Formula 3]

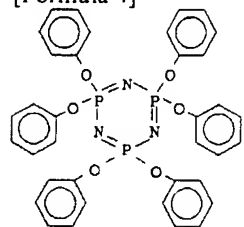


it is the compound shown by (n is the integer of 3-5 and R and R' shows the alkyl group or aryl group of carbon numbers 1-4 which may be different even if the same), and independent in 6 member rings of a trimer, 8 member rings of a tetramer, and 10 member rings of a pentamer -- or it can mix and use It is desirable to use a trimer as a principal component from the fluidity of an epoxy resin molding compound.

[0012] n R in the above-mentioned formula (I) and R' are the alkyl groups or aryl groups of carbon numbers 1-4 which may be different even if the same, for example, when n is the trimer 6 member ring of 3, R and R' becomes six substituents, and even if these are all the same, they may differ The aryl group from the thermal resistance of an epoxy resin molding compound and a damp-proof viewpoint is desirable. It is a hydroxyphenyl machine that it is especially a phenyl group desirable still more preferably. Although a hydroxyphenyl machine is sufficient as all of n R and n R' when introducing a hydroxyphenyl machine, 2-4 introduction is desirable. If the number of hydroxyphenyl machines becomes five or more pieces, an epoxy resin hardened material will tend to become weak, and in order that the component which is not incorporated by the structure of cross linkage of an epoxy resin may appear in less than two cases, thermal resistance tends to fall.

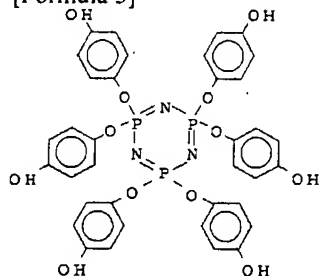
[0013] As desirable structure of the annular phosphazene compound of the (C) component used in this invention, it is for example, following formula (II) - (IV).

[Formula 4]



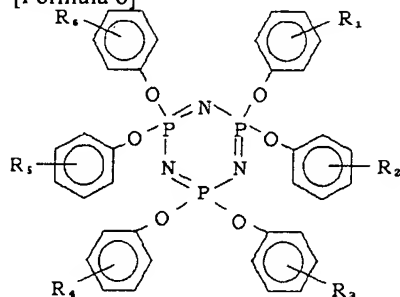
..... (II)

[Formula 5]



..... (III)

[Formula 6]



..... (IV)

(2-4 of R1-R6 pieces are a hydroxyl group, and other 4-2 pieces show hydrogen) etc. -- it is raised

[0014] The addition of these annular phosphazene compounds needs to be 0.2 - 3.0% of the weight of within the limits to all other combination components except a bulking agent. When fewer than 0.2 % of the weight, a fire-resistant effect is not demonstrated, but when it exceeds 3.0 % of the weight, a damp-proof fall is caused.

[0015] In this invention, the epoxy resin molding compound for fire-resistant electronic-parts closure of a non halogen and non antimony which excelled [ use / the specific annular phosphazene compound of the (C) component ] in reliability and the moldability is offered. Although it is generally known that combined use of a phosphorus compound and a nitride is good for flameproofing, this invention offers the compound which includes the both sides of a phosphorus atom and a nitrogen atom in structure as a flame-retarder component of the epoxy resin molding compound for semiconductor closure which can demonstrate the outstanding reliability.

[0016] Moreover, it is required to use an inorganic bulking agent from a viewpoint of hygroscopic reduction and the improvement in on the strength as a bulking agent. As a minerals bulking agent of the (D) component in this invention, single crystal fiber, such as fine particles, such as a fused silica, a crystal silica, an alumina, zircon, a calcium silicate, a calcium carbonate, a silicon carbide, boron nitride, a beryllia, and a zirconia, or a bead which globular-form-ized these, a potassium titanate, a silicon carbide, a silicon nitride, and an alumina, one or more kinds of glass fibers, etc. can be blended, and can be used. furthermore, as an inorganic bulking agent with a fire-resistant effect, an aluminum hydroxide, a magnesium hydroxide, a zinc borate, etc. are raised, and independent in these -- or it can also use together and use As loadings of a minerals bulking agent, 70 % of the weight or more is desirable from a viewpoint of reduction of hygroscopicity and coefficient of linear expansion, and the improvement in on the strength. In the above-mentioned inorganic bulking agent, the alumina from a viewpoint of high temperature conductivity [ fused silica / from a viewpoint of coefficient-of-linear-expansion reduction ] is desirable, and a bulking agent configuration has a desirable globular form from the point of the fluidity at the time of fabrication, and golden wearing-of-die nature.

[0017] Coupling agents, such as coloring agents, such as release agents, such as a higher fatty acid, a higher-fatty-acid metal salt, an ester system wax, and a polyolefine system wax, and carbon black, an epoxy silane, an amino silane, a ureido silane, a vinyl silane, an alkyl silane, organic titanate, and aluminum alcoholate, etc. can be used as other additives.

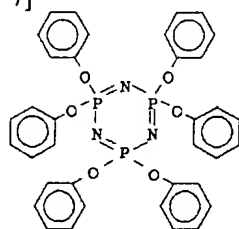
[0018] Although it can prepare no matter what technique it may use if the distributed mixture of the various raw materials can be carried out uniformly, after mixing the raw material of predetermined loadings enough by the mixer etc. as general technique and the molding material in this invention carries out melting kneading with a roll mill, an extruder, etc., it can mention the method of cooling and pulverizing.

[0019] Elements, such as passive elements, such as active elements, such as a semiconductor chip, a transistor, diode, and a thyristor, a capacitor, a resistor, and a coil, can be carried in supporter material, such as a leadframe, a tape carrier [ finishing / wiring ], a patchboard, glass, and a silicon wafer, a required portion can be closed by the molding material for closure of this invention, and electronic parts can be manufactured. TCP which closed the semiconductor chip connected to the tape carrier by the bump by the molding material of this invention as such electronic parts, for example can be mentioned. Moreover, the COB module which closed passive elements, such as active elements, such as the semiconductor chip and transistor which connected with the wiring formed on a patchboard or glass with wire bonding, flip chip bonding, solder, etc., diode, and a thyristor, and/or a capacitor, a resistor, and a coil, by the molding material of this invention, a hybrid IC, a multi chip module, etc. can be mentioned. As a method of closing electronic parts, although the low voltage transfer-molding method is the most common, you may use the injection fabricating method, compression forming, etc.

[0020]

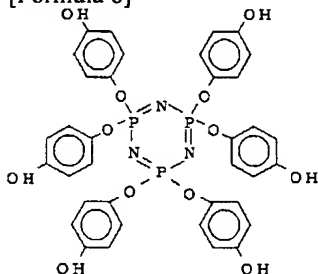
[Example] Next, although an example explains this invention, the range of this invention is not limited to these examples.

[0021] An example 1 - the 6 weight per epoxy equivalent 200, a cresol novolak type epoxy resin with a softening temperature of 67 degrees C, A weight per epoxy equivalent 188, the biphenyl skeleton type epoxy resin of 106 degrees C of melting points (- screw (2, 3-epoxy propoxy) -3, 3', and 4 and 4 '5, 5'-tetramethyl biphenyl), As a hydroxyl equivalent 106, a phenol novolak resin with a softening temperature of 83 degrees C, a hydroxyl equivalent 167, a phenol aralkyl resin (; made from 3 Ito \*\* MIREKKUSU XL- 225) with a softening temperature of 70 degrees C, triphenyl phosphine, carnauba wax, carbon black, and a coupling agent. The compound 1 which is the (C) component of this invention and is shown with the following structure expression as gamma-glycidoxypolytrimetoxysilane, a fused silica, and a flame retarder - a compound 3. [Formula 7]



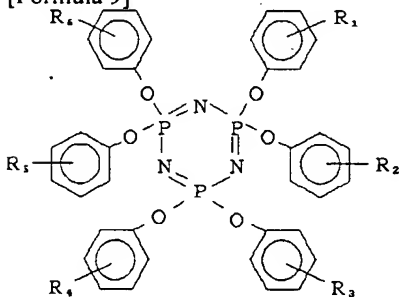
... 化合物 1

[Formula 8]



... 化合物 2

[Formula 9]



... 化合物 3

It blended by the weight ratio which shows in Table 1 (three of other R1-R6 pieces show hydrogen with a hydroxyl group in three pieces), roll kneading was performed on the kneading temperature of 80-90 degrees C, and the conditions for mixing-time 10 minutes, and the molding material of examples 1-6 was produced.

[0022] The molding material of the examples 1 and 2 of comparison was produced by the combination shown in Table 1 like the example except having used the bromine-ized bisphenol A type epoxy resin of a weight per epoxy equivalent 375, the softening temperature of 80 degrees C, and 48 % of the weight of bromine contents, and the antimony trioxide as the example 1 of comparison, and two flame retarders.

[0023]

[Table 1]

表1

項目	実施例						比較例	
	1	2	3	4	5	6	1	2
クレゾールノボラック型エポキシ樹脂	100	100	100	-	-	-	85	-
ビフェニル骨格型エポキシ樹脂	-	-	-	100	100	100	-	85
ブロム化エポキシ樹脂	-	-	-	-	-	-	15.0	15.0
フェノールノボラック樹脂	53.0	24.3	37.4	-	-	-	49.0	-
キシレン骨格樹脂	-	-	-	88.8	47.9	66.1	-	82.0
カルナバワックス	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
三酸化アンチモン	-	-	-	-	-	-	10.0	5.0
カーボンブラック	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
カップリング剤	3.0	3.0	3.0	4.5	4.5	4.5	3.0	4.5
トリフェニルメスフィン	1.5	1.5	1.5	1.5	2.5	2.5	1.5	2.5
化合物1	37.0	-	-	35.0	-	-	-	-
化合物2	-	35.8	-	-	32.3	-	-	-
化合物3	-	-	36.4	-	-	33.6	-	-
溶融シリカ*1	694	504	545	1322	1081	1191	501	1119
充填剤量(重量)	75%	75%	75%	85%	86%	85%	76%	85%
焼成度(重量)*2	2.5%	2.5%	2.5%	2.0%	2.0%	2.0%	-	-

\* 1: 平均粒径 17.5  $\mu$ m, 比表面積 1.5m<sup>2</sup>/g の破砕状溶融シリカ

\* 2: 充填剤を除く配合成分に対する焼成剤の焼成度(重量百分率)

[0024] The method of showing below the property of the molding material obtained in the example and the example of comparison estimated.

- (1) The metal mold which fabricates a disk with a degree-of-hardness diameter [ of 100mm ] and a thickness of 3mm at the time of heat was used, the molding material was fabricated with the transfer press on 180\*\*3 degrees C, 6.9\*\*0.17MPa, and the conditions for 90 seconds, and it asked for the degree of hardness by the Shore hardness tester (D type) at the time of the heat of the mold goods immediately after fabrication. In addition, it is estimated that the value of a degree of hardness is so good that a numeric value is high at the time of heat.
- (2) The with a diameter thickness [ based on water-absorption JIS-K -6911 / 3mm thickness of 50mm ] disk was produced, and it humidified on condition that 85 degrees C and 85%RH, and asked from the weight change after a predetermined time.
- (3) The molding material was fabricated with the transfer press on the aluminum foil of 30 micrometers of adhesive properties on 180\*\*3 degrees C, 6.9\*\*0.17MPa, and the conditions for 90 seconds, and the Peel intensity to the direction of 90 degrees of aluminum foil was measured after that.
- (4) The metal mold which fabricates a test piece with a fire-resistant thickness of 1/16 inch was used, the molding material was fabricated with the transfer press on 180\*\*3 degrees C, 6.9\*\*0.17MPa, and the conditions for 90 seconds, and 180\*\*5 degrees C and the 5-hour postcure were performed after that. Evaluation followed the UL94-V0 examining method.
- (5) The test element in which the aluminum wiring whose line / space are 10 micrometers was formed on the silicon substrate which has a 5-micrometer oxide film in the elevated-temperature neglect property appearance size 5x9 (mm) was used, it connected with the leadframe of 42 alloys which gave partial silver plating with a silver paste, and the bonding pad and inner lead of an element were connected by Au line by 200 degrees C by the thermostat sonic mold wire bonder. Then, 16 pin type DIP (Dual Inline Package) was produced by transfer molding, obtained IC for an examination was kept to the 200-degree C thermostat, it took out for every predetermined time, the continuity check was performed, and the poor number was investigated. In addition, fabrication of the IC package for evaluation fabricated the molding material with the transfer press on 180\*\*3 degrees C, 6.9\*\*0.17MPa, and the conditions for 90 seconds, and performed 180\*\*5 degrees C and the 5-hour postcure after that.

[0025] The obtained evaluation result is shown in Table 2.

[Table 2]

表2

項目	実施例						比較例	
	1	2	3	4	5	6	1	2
熱時硬度	78.0	86.0	84.0	75.0	83.0	81.0	85.0	80.0
吸水率 (72h) (%)	0.25	0.32	0.27	0.17	0.21	0.19	0.28	0.19
接着性 (N/m)	350	250	330	780	680	720	310	720
難燃性: UL94	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0
高温放置特性	200h	0/10	0/10	0/10	0/10	0/10	0/10	0/10
(不良数/母数)	400h	0/10	0/10	0/10	0/10	0/10	0/10	4/10
	600h	0/10	0/10	0/10	0/10	0/10	3/10	10/10
	800h	0/10	0/10	0/10	0/10	0/10	7/10	-

[0026] compared with the examples 1 and 2 of comparison containing a bromine-ized resin and an antimony compound, an elevated-temperature neglect property boils the examples 1-6 of this invention markedly, and is improving Since especially the examples 4-6 are using the biphenyl skeleton type epoxy resin, its adhesive property is also good. Although each example using the flame retarder of this invention has a good elevated-temperature neglect property and being excelled also in fire retardancy, since a compound 1 does not have an epoxy group and the functional group in which a reaction is possible, when this is used as a flame retarder, as shown in examples 1 and 4, a degree of hardness falls a little at the time of heat. Moreover,



since all of six substituents of a compound 2 are an epoxy group and the hydroxyphenyl machine in which a reaction is possible, although the hardenability of the examples 2 and 5 using this is good, an adhesive property falls a little. Especially the examples 3 and 6 that used the compound 3 whose three in a substituent are a hydroxyphenyl machine are excellent in a degree of hardness and adhesive balance at the time of heat.

[0027]

[Effect of the Invention] If the epoxy resin molding compound for electronic-parts closure obtained by this invention can attain flameproofing with a non halogen and non antimony as the example showed, and electronic parts, such as IC and LSI, are closed using this, its moldability is good, the product excellent in reliability, such as moisture resistance and an elevated-temperature neglect property, can be obtained, and the industrial value is size.

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[Translation done.]

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TECHNICAL FIELD

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[The technical field to which invention belongs] This inventions are an epoxy resin molding compound for semiconductor closure, especially the epoxy resin molding compound for electronic-parts closure of the non halogen system demanded from a viewpoint of environmental correspondence, and relate to the electronic parts which closed the element by the suitable molding material for closure of VLSI of which severe reliability, such as moisture resistance and reflow-proof crack nature, is required, and its molding material.

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PRIOR ART

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[Description of the Prior Art] From the former, the epoxy resin molding compound is widely used in the field of closure of elements for electronic parts, such as a transistor and IC. As this reason, it is because the epoxy resin maintains balance in many properties, such as an electrical property, moisture resistance, thermal resistance, a mechanical characteristic, and an adhesive property with an insertion article. Flameproofing of these epoxy resin molding compounds is mainly performed by the combination of bromine-ized resins, such as diglycidyl ether of tetrabromobisphenol A, and an antimony oxide.

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EFFECT OF THE INVENTION

---

[Effect of the Invention] If the epoxy resin molding compound for electronic-parts closure obtained by this invention can attain flameproofing with a non halogen and non antimony as the example showed, and electronic parts, such as IC and LSI, are closed using this, its moldability is good, the product excellent in reliability, such as moisture resistance and an elevated-temperature neglect property, can be obtained, and the industrial value is size.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] In recent years, it stems from the problem of dioxin from a viewpoint of environmental protection, a deca bromine is begun, and there is movement of regulation also about a halogenation resin. Similarly, an antimony compound also has the movement of regulation from a toxic field, and the demand of dehalogenation-izing (debromination) and the formation of \*\* antimony is coming out of it about the epoxy resin molding compound for electronic-parts closure. Moreover, it is known that bromine ion will have a bad influence on the elevated-temperature neglect property of the plastics closure IC, and reduction of the amount of bromine-ized resins is desired also from this viewpoint. this invention was made in view of this situation, and tends to offer the epoxy resin material for electronic-parts closure which was excellent in the elevated-temperature storage property.

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[Translation done.]

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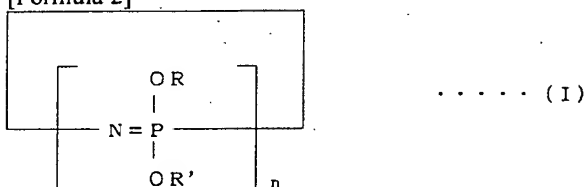
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## MEANS

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, as a result of repeating examination wholeheartedly, by blending a specific annular phosphazene compound as a flame retarder, artificers find out that the above-mentioned purpose can be attained and came to complete this invention.

[0005] That is, this invention is the epoxy resin which has two or more epoxy groups in (1) (A) 1 molecule, the compound which has two or more phenolic hydroxyl groups in (B) 1 molecule, and the (C) following formula (I).

[Formula 2]



the annular phosphazene compound shown by (n is the integer of 3-5 and R and R' shows the alkyl group or aryl group of carbon numbers 1-4 which may be different even if the same) -- (D) It is the molding material which uses an inorganic bulking agent as an indispensable component, and the content of the (C) component is an amount from which the amount of a phosphorus atom becomes 0.2 - 3.0 % of the weight to the total quantity of the combination component except a bulking agent (D). (D) The epoxy resin molding compound for electronic-parts closure to which the content of a component is characterized by being 70 % of the weight or more to the whole molding material, (2) The epoxy resin molding compound for electronic-parts closure of the above-mentioned (1) publication whose n of the (C) component is 3, (3) The above (1) all of n R of the (C) component and whose n R' are phenyl groups, or the epoxy resin molding compound for electronic-parts closure given in (2), (4) 2-4 in n R of the (C) component and n R' are a hydroxyphenyl machine. The above (1) other all of whose are phenyl groups, or the epoxy resin molding compound for electronic-parts closure given in (2), (5) The above (1) all of n R of the (C) component and whose n R' are hydroxyphenyl machines, or the epoxy resin molding compound for electronic-parts closure given in (2), (6) One epoxy resin molding compound for electronic-parts closure of the above-mentioned (1) - (5) publications whose epoxy resins of the (A) component are - screw (2, 3-epoxy propoxy) -3, 3', and 4 and 4 '5, 5'-tetramethyl biphenyls, (7) -- the electronic parts which close an element by one epoxy resin molding compound for electronic-parts closure of the above-mentioned (1) - (6) publications, and are obtained -- it comes out

[0006]

[Embodiments of the Invention] As an epoxy resin of the (A) component used in this invention Although it is generally used by the epoxy resin molding compound for electronic-parts closure and there is especially no limitation, for example That which epoxidated the novolak resin of phenols including a phenol novolak type epoxy resin and an orthochromatic cresol novolak type epoxy resin, and aldehydes, Diglycidyl ether, such as bisphenol A, Bisphenol F, Bisphenol S, and alkylation biphenol, The glycidyl amine type epoxy resin obtained by the reaction of polyamine and epichlorohydrin, such as a diamino diphenylmethane and an isocyanuric acid the line oxidized and obtained by peroxy acids, such as a peracetic acid, in olefin combination -- there are an aliphatic epoxy resin, an alicycle group epoxy resin, etc., and any number of kinds of these can be suitably used together

[0007] In the epoxy resin shown above, when alkylation biphenol type diepoxy resins, such as a - screw (2, 3-epoxy propoxy) -3, 3', and 4 and 4 '5, 5'-tetramethyl biphenyl, are used, an adhesive property and hygroscopicity are good, and the molding material which was excellent in reflow-proof crack nature and moisture resistance by this is obtained. As for this alkylation biphenol type diepoxy resin, it is desirable to use it 60% of the weight or more to the epoxy resin whole quantity. At less than 60 % of the weight, the low hygroscopicity of the epoxy resin concerned and the feature of a high adhesive property are not demonstrated, but an effect is small to the solder-proof nature which is the purpose of this invention. What epoxidates a - screw hydroxy 3, 3', and 4 and 4 '5, 5'-tetramethyl biphenyl, using epichlorohydrin as the epoxy resin concerned, and is obtained is raised.

[0008] As a compound which has two or more phenolic hydroxyl groups in 1 molecule of the (B) component used in this invention A phenol, cresol, a xylenol, a resorcinol, a catechol, Phenols or alpha naphthols, such as bisphenol A and Bisphenol F, Naphthols, formaldehyde, such as a beta naphthol and dihydroxy naphthalene, Aldehydes, such as an acetaldehyde, a propionaldehyde, a benzaldehyde, and a salichlaldehyde, under an acid catalyst Condensation or the resin which is made to

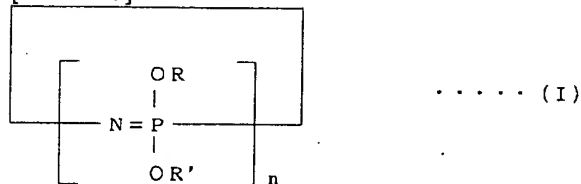
carry out copolycondensation and is obtained, there are PORIPA rabbi nil phenol resin, a phenol aralkyl resin which has the KISHIRIREN machine compounded from phenols and dimethoxy paraxylene, and independent -- or you may use two or more kinds together

[0009] (A) although especially limitation is not carried out for the equivalent ratio (the number of epoxy groups of number of (B) ] of hydroxyl groups/(A)) of the epoxy resin of a component, and the phenolic compound of the (B) component -- each -- unreacted -- a part -- in order to stop few, it is desirable to set it as the range of 0.7-1.3

[0010] Moreover, the hardening accelerator which promotes the hardening reaction of an epoxy resin and phenol resin can be used if needed. As this hardening accelerator, for example A diazabicyclo alkene and its derivatives, such as 1 and 8-diazabicyclo (5, 4, 0) undecene -7, A triethylenediamine, a benzyl dimethylamine, a triethanolamine, The third class amines, such as dimethylamino ethanol and a tris (dimethyl aminomethyl) phenol, 2-methyl imidazole, 2-phenyl imidazole, a 2-phenyl-4-methyl imidazole, Imidazole derivatives, such as 2-heptadecyl imidazole, tributyl phosphine, Organic phosphines, such as methyl diphenylphosphine and triphenyl phosphine Tetrapod substitution phosphonium tetrapod substitution borate, such as tetrapod phenyl phosphonium tetraphenyl borate, There are tetraphenylboron salts, such as 2-ethyl-4-methyl imidazole tetraphenyl borate and N-methyl morpholine tetraphenyl borate, etc.

[0011] The annular phosphazene compound of the (C) component used as a flame retarder in this invention is the following formula (I).

[Formula 3]

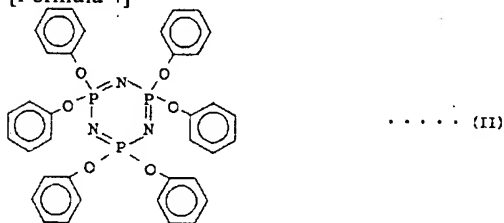


it is the compound shown by (n is the integer of 3-5 and R and R' shows the alkyl group or aryl group of carbon numbers 1-4 which may be different even if the same), and independent in 6 member rings of a trimer, 8 member rings of a tetramer, and 10 member rings of a pentamer -- or it can mix and use It is desirable to use a trimer as a principal component from the fluidity of an epoxy resin molding compound.

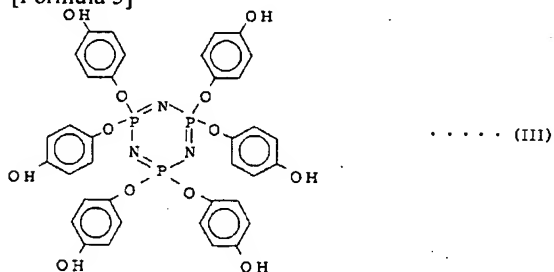
[0012] n R in the above-mentioned formula (I) and R' are the alkyl groups or aryl groups of carbon numbers 1-4 which may be different even if the same, for example, when n is the trimer 6 member ring of 3, R and R' becomes six substituents, and even if these are all the same, they may differ The aryl group from the thermal resistance of an epoxy resin molding compound and a damp-proof viewpoint is desirable. It is a hydroxyphenyl machine that it is especially a phenyl group desirable still more preferably. Although a hydroxyphenyl machine is sufficient as all of n R and n R' when introducing a hydroxyphenyl machine, 2-4 introduction is desirable. If the number of hydroxyphenyl machines becomes five or more pieces, an epoxy resin hardened material will tend to become weak, and in order that the component which is not incorporated by the structure of cross linkage of an epoxy resin may appear in less than two cases, thermal resistance tends to fall.

[0013] As desirable structure of the annular phosphazene compound of the (C) component used in this invention, it is for example, following formula (II) - (IV).

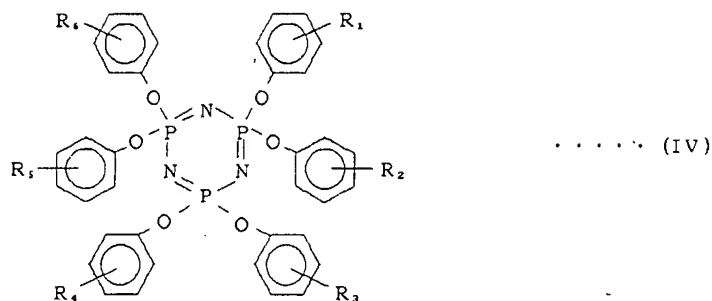
[Formula 4]



[Formula 5]



[Formula 6]



(2-4 of R1-R6 pieces are a hydroxyl group, and other 4-2 pieces show hydrogen) etc. -- it is raised

[0014] The addition of these annular phosphazene compounds needs to be 0.2 - 3.0% of the weight of within the limits to all other combination components except a bulking agent. When fewer than 0.2 % of the weight, a fire-resistant effect is not demonstrated, but when it exceeds 3.0 % of the weight, a damp-proof fall is caused.

[0015] In this invention, the epoxy resin molding compound for fire-resistant electronic-parts closure of a non halogen and non antimony which excelled [ use / the specific annular phosphazene compound of the (C) component ] in reliability and the moldability is offered. Although it is generally known that combined use of a phosphorus compound and a nitride is good for flameproofing, this invention offers the compound which includes the both sides of a phosphorus atom and a nitrogen atom in structure as a flame-retarder component of the epoxy resin molding compound for semiconductor closure which can demonstrate the outstanding reliability.

[0016] Moreover, it is required to use an inorganic bulking agent from a viewpoint of hygroscopic reduction and the improvement in on the strength as a bulking agent. As a minerals bulking agent of the (D) component in this invention, single crystal fiber, such as fine particles, such as a fused silica, a crystal silica, an alumina, zircon, a calcium silicate, a calcium carbonate, a silicon carbide, boron nitride, a beryllia, and a zirconia, or a bead which globular-form-ized these, a potassium titanate, a silicon carbide, a silicon nitride, and an alumina, one or more kinds of glass fibers, etc. can be blended, and can be used. furthermore, as an inorganic bulking agent with a fire-resistant effect, an aluminum hydroxide, a magnesium hydroxide, a zinc borate, etc. are raised, and independent in these -- or it can also use together and use As loadings of a minerals bulking agent, 70 % of the weight or more is desirable from a viewpoint of reduction of hygroscopicity and coefficient of linear expansion, and the improvement in on the strength. In the above-mentioned inorganic bulking agent, the alumina from a viewpoint of high temperature conductivity [ fused silica / from a viewpoint of coefficient-of-linear-expansion reduction ] is desirable, and a bulking agent configuration has a desirable globular form from the point of the fluidity at the time of fabrication, and golden wearing-of-die nature.

[0017] Coupling agents, such as coloring agents, such as release agents, such as a higher fatty acid, a higher-fatty-acid metal salt, an ester system wax, and a polyolefine system wax, and carbon black, an epoxy silane, an amino silane, a ureido silane, a vinyl silane, an alkyl silane, organic titanate, and aluminum alcoholate, etc. can be used as other additives.

[0018] Although it can prepare no matter what technique it may use if the distributed mixture of the various raw materials can be carried out uniformly, after mixing the raw material of predetermined loadings enough by the mixer etc. as general technique and the molding material in this invention carries out melting kneading with a roll mill, an extruder, etc., it can mention the method of cooling and pulverizing.

[0019] Elements, such as passive elements, such as active elements, such as a semiconductor chip, a transistor, diode, and a thyristor, a capacitor, a resistor, and a coil, can be carried in supporter material, such as a leadframe, a tape career [ finishing / wiring ], a patchboard, glass, and a silicon wafer, a required portion can be closed by the molding material for closure of this invention, and electronic parts can be manufactured. TCP which closed the semiconductor chip connected to the tape career by the bump by the molding material of this invention as such electronic parts, for example can be mentioned. Moreover, the COB module which closed passive elements, such as active elements, such as the semiconductor chip and transistor which connected with the wiring formed on a patchboard or glass with wire bonding, flip chip bonding, solder, etc., diode, and a thyristor, and/or a capacitor, a resistor, and a coil, by the molding material of this invention, a hybrid IC, a multi chip module, etc. can be mentioned. As a method of closing electronic parts, although the low voltage transfer-molding method is the most common, you may use the injection fabricating method, compression forming, etc.

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[Translation done.]



## \* NOTICES \*

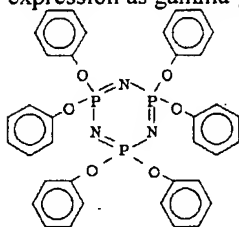
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## EXAMPLE

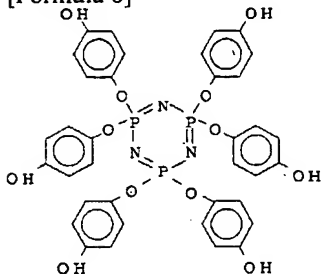
[Example] Next, although an example explains this invention, the range of this invention is not limited to these examples.

[0021] An example 1 - the 6 weight per epoxy equivalent 200, a cresol novolak type epoxy resin with a softening temperature of 67 degrees C, A weight per epoxy equivalent 188, the biphenyl frame type epoxy resin of 106 degrees C of melting points (- screw (2, 3-epoxy propoxy) -3, 3', and 4 and 4 '5, 5'-tetramethyl biphenyl), As a hydroxyl equivalent 106, a phenol novolak resin with a softening temperature of 83 degrees C, a hydroxyl equivalent 167, a phenol aralkyl resin (; made from 3 Ito \*\* MIREKKUSU XL- 225) with a softening temperature of 70 degrees C, triphenyl phosphine, carnauba wax, carbon black, and a coupling agent. The compound 1 which is the (C) component of this invention and is shown with the following structure expression as gamma-glycidoxypolytrimetoxysilane, a fused silica, and a flame retarder - a compound 3. [Formula 7]



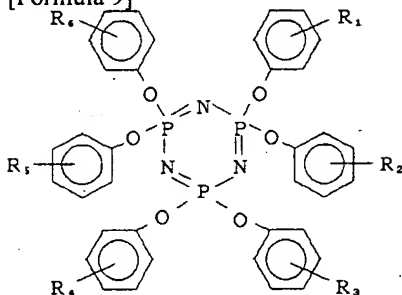
... 化合物 1

[Formula 8]



... 化合物 2

[Formula 9]



... 化合物 3

It blended by the weight ratio which shows in Table 1 (three of other R1-R6 pieces show hydrogen with a hydroxyl group in three pieces), roll kneading was performed on the kneading temperature of 80-90 degrees C, and the conditions for mixing-time 10 minutes, and the molding material of examples 1-6 was produced.

[0022] The molding material of the examples 1 and 2 of comparison was produced by the combination shown in Table 1 like the example except having used the bromine-ized bisphenol A type epoxy resin of a weight per epoxy equivalent 375, the softening temperature of 80 degrees C, and 48 % of the weight of bromine contents, and the antimony trioxide as the example 1 of comparison, and two flame retarders.

[0023]

[Table 1]

表1

項目	実施例						比較例	
	1	2	3	4	5	6	1	2
クレゾールノボラック型エポキシ樹脂	100	100	100	-	-	-	85	-
ビフェニル骨格型エポキシ樹脂	-	-	-	100	100	100	-	85
ブロム化エポキシ樹脂	-	-	-	-	-	-	15.0	15.0
フェノールノボラック樹脂	53.0	24.3	37.4	-	-	-	49.0	-
キシリル骨格樹脂	-	-	-	88.8	47.9	66.1	-	62.0
カルナバワックス	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
三酸化アンチモン	-	-	-	-	-	-	10.0	5.0
カーボンブラック	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
カップリング剤	3.0	3.0	3.0	4.5	4.5	4.5	3.0	4.5
トリフェニルメスフィン	1.5	1.5	1.5	1.5	2.5	2.5	1.5	2.5
化合物1	37.0	-	-	35.0	-	-	-	-
化合物2	-	35.8	-	-	32.3	-	-	-
化合物3	-	-	36.4	-	-	33.6	-	-
溶融シリカ*1	694	504	545	1322	1081	1191	501	1119
充填剤量(重量)	75%	75%	75%	85%	85%	85%	75%	85%
焼成度(重量)*2	2.5%	2.5%	2.5%	2.0%	2.0%	2.0%	-	-

\* 1: 平均粒径17.5 $\mu$ m、比表面積1.5m<sup>2</sup>/gの破砕状溶融シリカ

\* 2: 充填剤を除く配合成分に対する焼成剤の焼成度(重量百分率)

[0024] The method of showing below the property of the molding material obtained in the example and the example of comparison estimated.

(1) The metal mold which fabricates a disk with a degree-of-hardness diameter [ of 100mm ] and a thickness of 3mm at the time of heat was used, the molding material was fabricated with the transfer press on 180\*\*3 degrees C, 6.9\*\*0.17MPa, and the conditions for 90 seconds, and it asked for the degree of hardness by the Shore hardness tester (D type) at the time of the heat of the mold goods immediately after fabrication. In addition, it is estimated that the value of a degree of hardness is so good that a numeric value is high at the time of heat.

(2) The with a diameter thickness [ based on water-absorption JIS-K -6911 / 3mm thickness of 50mm ] disk was produced, and it humidified on condition that 85 degrees C and 85%RH, and asked from the weight change after a predetermined time.

(3) The molding material was fabricated with the transfer press on the aluminum foil of 30 micrometers of adhesive properties on 180\*\*3 degrees C, 6.9\*\*0.17MPa, and the conditions for 90 seconds, and the Peel intensity to the direction of 90 degrees of aluminum foil was measured after that.

(4) The metal mold which fabricates a test piece with a fire-resistant thickness of 1/16 inch was used, the molding material was fabricated with the transfer press on 180\*\*3 degrees C, 6.9\*\*0.17MPa, and the conditions for 90 seconds, and 180\*\*5 degrees C and the 5-hour postcure were performed after that. Evaluation followed the UL94-V0 examining method.

(5) The test element in which the aluminum wiring whose line / space are 10 micrometers was formed on the silicon substrate which has a 5-micrometer oxide film in the elevated-temperature neglect property appearance size 5x9 (mm) was used, it connected with the leadframe of 42 alloys which gave partial silver plating with a silver paste, and the bonding pad and inner lead of an element were connected by Au line by 200 degrees C by the thermostat sonic mold wire bonder. Then, 16 pin type DIP (Dual Inline Package) was produced by transfer molding, obtained IC for an examination was kept to the 200-degree C elevated-temperature tub, it took out for every predetermined time, the continuity check was performed, and the poor number was investigated. In addition, fabrication of the IC package for evaluation fabricated the molding material with the transfer press on 180\*\*3 degrees C, 6.9\*\*0.17MPa, and the conditions for 90 seconds, and performed 180\*\*5 degrees C and the 5-hour postcure after that.

[0025] The obtained evaluation result is shown in Table 2.

[Table 2]

表2

項目	実施例						比較例	
	1	2	3	4	5	6	1	2
熱時硬度	78.0	86.0	84.0	75.0	83.0	81.0	85.0	80.0
吸水率 (72h) (%)	0.25	0.32	0.27	0.17	0.21	0.19	0.28	0.18
接着性 (N/m)	350	250	330	780	580	720	310	720
難燃性: UL94	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0
高温放置特性	200h	0/10	0/10	0/10	0/10	0/10	0/10	0/10
(不良数/母数)	400h	0/10	0/10	0/10	0/10	0/10	0/10	4/10
	600h	0/10	0/10	0/10	0/10	0/10	3/10	10/10
	800h	0/10	0/10	0/10	0/10	0/10	7/10	-

[0026] compared with the examples 1 and 2 of comparison containing a bromine-ized resin and an antimony compound, an elevated-temperature neglect property boils the examples 1-6 of this invention markedly, and is improving Since especially the examples 4-6 are using the biphenyl frame type epoxy resin, its adhesive property is also good. Although each example using the flame retarder of this invention has a good elevated-temperature neglect property and being excelled also in fire retardancy, since a compound 1 does not have an epoxy group and the functional group in which a reaction is possible, when this is used as a flame retarder, as shown in examples 1 and 4, a degree of hardness falls a little at the time of heat. Moreover,

since all of six substituents of a compound 2 are an epoxy group and the hydroxyphenyl machine in which a reaction is possible, although the hardenability of the examples 2 and 5 using this is good, an adhesive property falls a little. Especially the examples 3 and 6 that used the compound 3 whose three in a substituent are a hydroxyphenyl machine are excellent in a degree of hardness and adhesive balance at the time of heat.

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[Translation done.]